

Electrochemical Synthesis and Characterization of Poly(pyrrole-co- ϵ -caprolactone) Conducting Copolymer

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ABSTRACT: The direct electrochemical copolymerization of pyrrole (Py) and ϵ -caprolactone at various monomer ratios was carried out by potentiostatic methods in nitromethane. Characterizations of the novel copolymer were based on scanning electron microscopy, differential scanning calorimetry, thermal gravimetric analysis, cyclic voltammetry, electrochemical impedance spectroscopy, Fourier transform infrared spectra, and elemental analysis studies. The results showed that the electrochemical oxidation of Py and ϵ -caprolactone comonomers

generated true copolymers rather than blends of the two homopolymers. The electrical conductivity of the copolymers increased with the amount of polypyrrole in the copolymer between the value of 8.2 S/cm and 0.6 S/cm. A probable mechanism of copolymerization was proposed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1070–1075, 2009

Key words: polypyrrole; electrochemical copolymerization; ϵ -caprolactone; copolymer; conducting polymer

INTRODUCTION

In recent years, conducting polymers have received a great deal of attention because of their potential applications in the fields of sensors and biosensors, electrochromic displays, light-emitting devices, secondary batteries, etc.^{1–9} However, many kinds of conducting polymers, such as polypyrrole (PPy) and polyaniline, are limited in practical use because of their poor mechanical properties and processability.^{10,11} To compensate for these certain deficiencies, the use of surfactants as additive in the electrolyte solution,^{12,13} the synthesis of conducting polymer composites, and copolymers combining an insulating polymer matrix were shown to be effective methods.^{14–20} In fact, these composites and copolymers sometimes exhibited some special properties such as compatibility and permselectivity.^{21,22} Generally speaking, the composites show a simple preparation process, but their stability was limited because of the loss of conductivity with aging. The copolymers

usually exhibit more stable chemical properties than the composites. Several kinds of copolymer containing pyrrole (Py) and other insulating units, such as tetrahydrofuran (THF), methyl methacrylate, ϵ -caprolactone, acryloyl chloride, etc., have been prepared and studied.^{17,23–27} All results showed the success in improving the mechanical and physical properties of PPy; in addition, an increase in the thermal stability of the copolymer was also observed.²³ However, these synthetic methods contained many reaction steps and strict conditions, leading to limited application of these copolymers.

Direct electrochemical copolymerization of monomers mixture in proper solution is a simple and effective method for the synthesis of conducting copolymers.^{28–30} The composition and thickness of copolymer films can be controlled by the ratios of monomers, applied potential, and the charge passed. However, few references^{31,32} reported the synthesis of the conducting–insulating copolymers by this method. Jin et al.³¹ synthesized a copolymer of Py and styrene directly on the surface of electrode. In our previous work, ring-opening copolymerization of Py and propylene was carried out by this technology.³² In this context, poly(ϵ -caprolactone) (PCL) was selected for insulating matrix of PPy-based copolymers as PCL behaves a good processability and biocompatibility. The novel copolymer of Py and ϵ -caprolactone was characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), cyclic voltammetry (CV), electrochemical

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impedance spectroscopy (EIS), Fourier transform infrared (FTIR) spectra, and elemental analysis.

EXPERIMENTAL

Py (Aldrich, St. Louis, MO) and ϵ -caprolactone were distilled under a nitrogen atmosphere at reduced pressure and then kept in refrigerator. PCL was synthesized by rare earth catalyst.³³ Nitromethane was first dried for 24 h in the presence of anhydrous magnesium sulfate, and then filtered, distilled, and stored with activated molecular sieves. Bu_4NBF_4 (Aldrich) was used as received.

All electrochemical experiments were carried out in one-compartment, three-electrode cell with CHI660 electrochemical workstation (CHI, China) at room temperature. Indium-tin oxide (ITO)-conducting glass plates ($1 \times 5 \text{ cm}^2$) were used as working electrode, Pt wire was used as a counter electrode, and Ag/AgCl (saturated KCl) was used as the reference electrode. Potentiostatic method was utilized for direct electrochemical polymerization of Py and CL. Nitromethane was used as the solvent³⁴ and Bu_4NBF_4 was used as the supporting electrolyte. Each solution was degassed by bubbling dry argon before the experiments, and a slight argon overpressure was maintained during the experiments.

Having been washed well with acetone for the removal of the solvent, the copolymer films were stripped from the electrodes and were extracted with CH_2Cl_2 for 1 day, and then dried in vacuum at room temperature. The conductivity of the polymer was measured by a four-probe method. FTIR spectra of the copolymers were measured on a pressed pellet with KBr, employing a Tensor 27 spectrometer (Bruker, Germany). Micrographs were obtained with a XL-30E SEM (Philips, Netherlands). Elemental analysis (C, H, and N) was carried out on a 240C elemental analyzer. Thermal behaviors of the polymers were analyzed by DSC (Netzsch STA 409PC) and TGA (SDT Q600). EIS measurements were conducted using an Autolab/PGSTAT30 (Eco Chemie, The Netherlands) with a three-electrode system.

RESULTS AND DISCUSSION

Electrochemical polymerization of Py and CL

Figure 1 shows the anodic polarization curves of Py (a), CL (b), and their mixture (c) in nitromethane solution. The curve for 0.1M Py has a threshold at 0.7 V, which indicates that Py is oxidized into radical cations and polymerized above 0.7 V. However, the curve for 1.5M CL is hardly changed under the same conditions. Moreover, after 1.5M CL nitromethane solution was electrolyzed at a constant potential of 1.8 V for about 1 h, no polymer product was

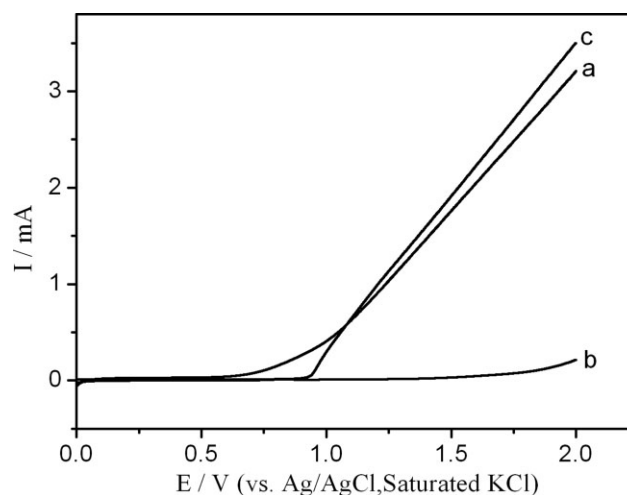


Figure 1 Anodic polarization curves of (a) 0.1M Py, (b) 1.5M CL, and (c) the mixture of 0.1M Py and 1.5M CL in nitromethane containing 0.05M Bu_4NBF_4 at a scan rate of 20 mV/s.

obtained. All these results suggest that pure CL cannot be homopolymerized on ITO electrode surface at the potentials lower than 2.0 V. The curve for the mixture of 0.1M Py and 1.5M CL shows a threshold value at 1.0 V, which implies that polymerization can occur in a mixture solution of Py and CL.

A black free-standing film was obtained on an ITO electrode during the electrochemical copolymerization of Py and CL. The film was flexible and easily peeled off from the electrode surface. The mechanical strength of copolymer was obviously better than that of pure PPy through tension test. The composition and conductivity of copolymer were observed to vary with the ratio of Py to CL in the polymerization solution (Table I). When the concentration of CL was increased from 0.1 to 2.0M, whereas Py was fixed at 0.1M, the ratio of Py/CL units in the copolymer decreased from 31.0 to 1.37 and the conductivity decreased from 8.2 to 0.6 S/cm. On the other hand, the conductivity of pure PPy prepared under same condition was 17.5 S/cm. The value is lower than that of reported in literature (69 S/cm),³⁴ which is probably due to the electrochemical overoxidation of PPy under high potential in solution.³⁵ However, the experiment showed that high potential is benefit to the formation of PCL units in copolymer. Considering the conductivity and mechanical properties of the copolymer, the potential 1.8 V and the mixture of 1.5M CL and 0.1 Py were chosen for the preparation of Py-CL copolymer in the further experiments.

The FTIR analysis and morphologies of the polymer films

Figure 2 shows the FTIR spectra of PPy, PCL, and the Py-CL copolymer synthesized potentiostatically

TABLE I
Composition (Py/CL) and Conductivity of Py-CL Copolymer Prepared Potentiostatically at 1.8 V in Nitromethane Containing 0.05 M Bu₄NBF₄

Concentration of monomer (mol/L)		Elemental analysis for the copolymers			(Py/CL) (molar ratio)	Conductivity σ (S/cm)
C _{py}	C _{CL}	%N	%C	%H		
0.1	0	13.61	52.13	4.01	–	17.5
0.1	0.1	13.34	47.95	3.36	31.0	8.2
0.1	0.6	13.19	48.02	3.39	24.3	3.8
0.1	1.0	12.72	47.8	3.27	15.6	2.0
0.1	1.5	8.06	51.49	5.62	1.74	0.8
0.1	2.0	7.5	53.8	6.23	1.37	0.6

at 1.8 V. The spectrum of PCL (Curve b) shows $-\text{CH}_2-$ stretching bands at 2855 and 2940 cm^{-1} , and C=O stretching band at 1730 cm^{-1} . According to the spectrum of PPy shown in Figure 2(a), there is neither significant band at 2800–3000 cm^{-1} nor at 1730 cm^{-1} . However, it shows strong bands at about 1140 and 1040 cm^{-1} , which are assigned to an in-plane deformation vibration of Py ring and a skeletal vibration of Py ring at about 1540 cm^{-1} .³⁶ In the spectrum of the Py-CL copolymer [Fig. 2(c,d)], strong bands appear at about 2855, 2930, 1730, 1040, and 1540 cm^{-1} . This indicates that the product contains both PCL and PPy matrix. In addition, the band at about 750 cm^{-1} (corresponding to BF_4^-) is decreased with increase in the content of PCL units in copolymer [Fig. 2(c,d)], which is probably due to the decrease in conductivity after introducing insulating PCL units into PPy matrix.

The surface appearance of Py-CL copolymer film was studied by SEM (Fig. 3). The pure PPy film shows a globular surface morphology [Fig. 3(a)]. The Py-CL copolymer prepared potentiostatically at 1.8 V reveals different appearance at the solution and electrode sides. The electrode side of the copolymer has a densely packed and smooth surface morphology [Fig. 3(b)]. The solution side of copolymer shows holothurian-like structure [Fig. 3(c,d)], which becomes denser than the surface of pure PPy. This implies that the growth mechanism for the Py-CL copolymer is different from that for PPy.

Electrochemical behavior and thermal properties of the polymer films

For observing the electrochemical behavior of the polymer films, the films deposited potentiostatically at 1.8 V for 60 s were used. The CVs of polymer films were recorded by reversibly cycling the potentials in monomer-free background electrolyte to obtain a stable CV pattern (Fig. 4). The CV of Py-CL copolymer was found to be obviously different from that of pure PPy. A couple of redox peaks (oxidation

peak 0.88 V and reduction peak -0.24 V) were observed for PPy. The redox potentials are positively shifted in comparison with those of PPy in organic and aqueous solutions,³⁷ which is results from the partial overoxidation and thick film of PPy. However, two oxidation peaks (0.77 V, 1.15 V) and a reduction peak (-0.07 V) were found for the Py-CL copolymer. This result strongly suggests that the electrochemical oxidation of Py and CL comonomers generated true copolymers rather than blends of the two kinds of homopolymers.

EIS has been proved to be a powerful and convenient tool for investigating electrode process by monitoring impedance and it can offer a lot of information about the electrode interfacial properties such as charge transfer resistance (R_{CT}) and double-layer capacitance (C_{dl}). EIS measurements were performed in nitromethane solution containing 0.05M Bu₄NBF₄. The amplitude of the applied sine-wave potential was 5 mV. The impedance measurements

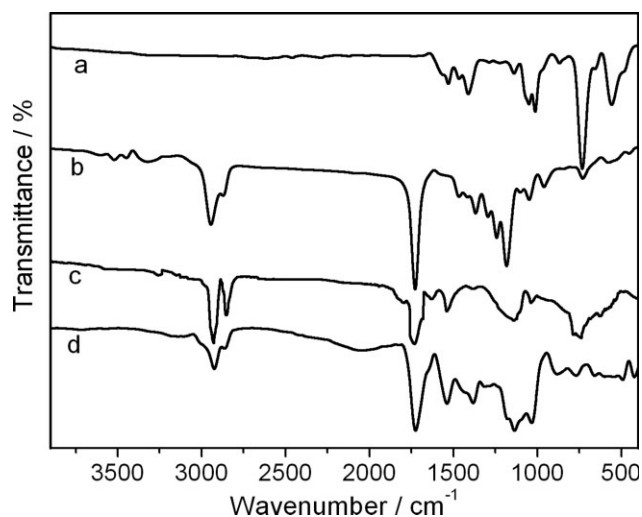


Figure 2 FTIR spectra of (a) PPy synthesized potentiostatically at 1.8 V in CH_3NO_2 containing 0.1M Py and 0.05M Bu₄NBF₄, (b) PCL and Py-CL copolymer prepared potentiostatically at 1.8 V in CH_3NO_2 containing 0.1M Py and various CL concentration: (c) 0.6M and (d) 1.5M.

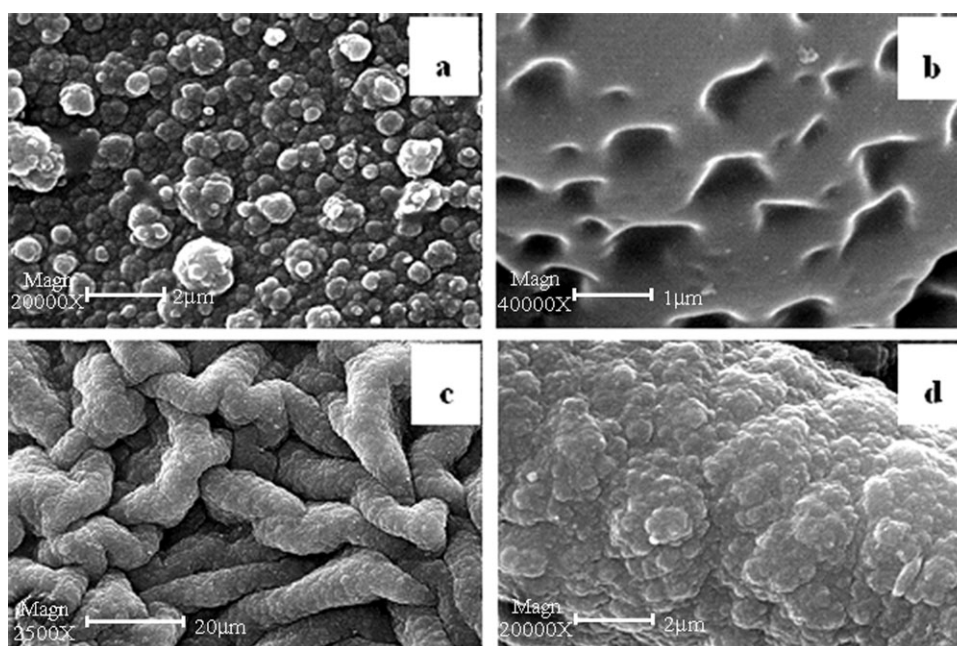


Figure 3 SEM photographs of (a) PPy, (b) the electrode side of Py-CL copolymer, (c) the solution side of Py-CL copolymer ($\times 2500$), and (d) the solution side of Py-CL copolymer ($\times 20,000$).

were recorded at a bias potential of 0 mV within the frequency range of 0.05 Hz–10 kHz. Figure 5 displays the Nyquist plots of the impedance spectroscopy for PPy and Py-CL copolymer. A semicircle located in the range of high frequencies and a nearly vertical response at low frequencies, which indicated that the electrode process is controlled by electrochemical reaction at high frequencies and by mass transfer at low frequencies. The intercept of the semicircle with the $Re(Z')$ axis at high frequencies is equal to the ohmic resistance of the solution and film, which is about 326 Ω both for PPy and for copolymer. The Nyquist diameter of the electrode

deposited with the Py-CL copolymer (Curve b, R_{CT} ca. 1420 Ω) is much larger than that of pure PPy (Curve a, R_{CT} ca. 380 Ω). This may have been caused by the hindrance of the insulating CL units in copolymer to the charge transfer.

In fact, the glass transition temperature (T_g) of pure PCL is -60°C ²⁴ and PPy prepared electrochemically does not show glass transition because of the rigid chains and crosslinkage. Thus, the DSC thermograms for the copolymer and pure PCL were obtained via heating from -100 to 100°C at a rate of $4^\circ\text{C}/\text{min}$. The DSC curve shows a glass transition (-60°C) and a melting peak (62°C) for pure PCL

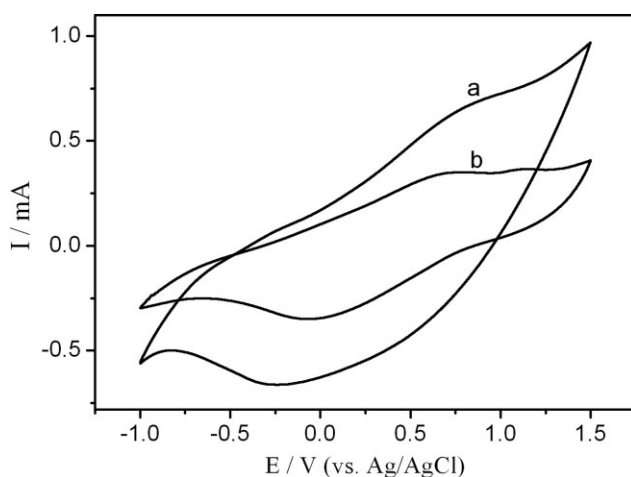


Figure 4 Cyclic voltammogram of (a) PPy and (b) Py-CL copolymer film in nitromethane containing 0.05M Bu_4NBF_4 at scan rate 100 mV/s.

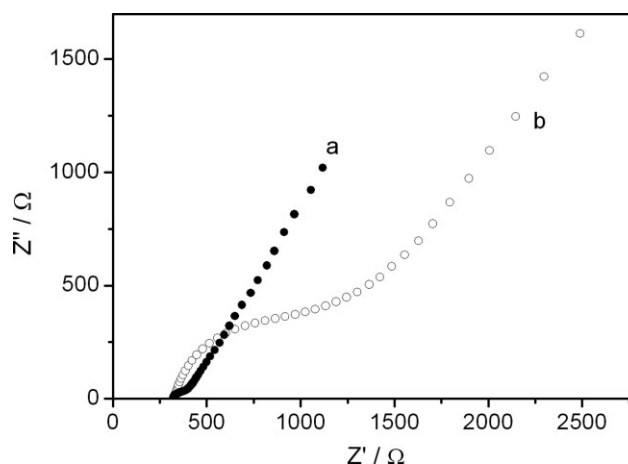


Figure 5 Nyquist plots of the electrochemical impedance spectroscopy (EIS) for (a) PPy and (b) Py-CL copolymer.

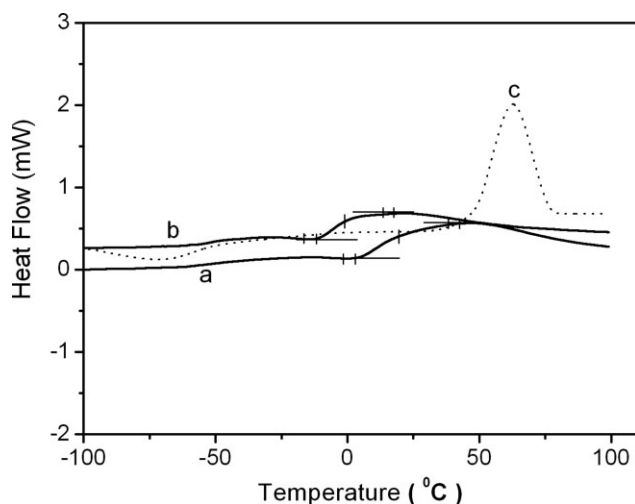


Figure 6 DSC curves of pure PCL (c) and Py-CL copolymer prepared potentiostatically at 1.8 V in CH_3NO_2 containing 0.1M Py, 1.5M CL, and 0.05M Bu_4NBF_4 for (a) 5 min and (b) 15 min.

[Fig. 6(c)]. Figure 6(a,b) shows the DSC curves of the copolymer obtained by electrochemical polymerization for various time. Disappearance of melting peak showed no crystallinity of copolymer, which is probably ascribed to the reduced segmental mobility of PCL matrix. The glass transition at 19 and -1°C were observed for the copolymer prepared for 5 and 15 min, respectively. This indicates that the content of PCL segment in the copolymer increases with the polymerization time, resulting in the decrease in T_g of the copolymer. The glass transition of products is a further proof of copolymer formation.

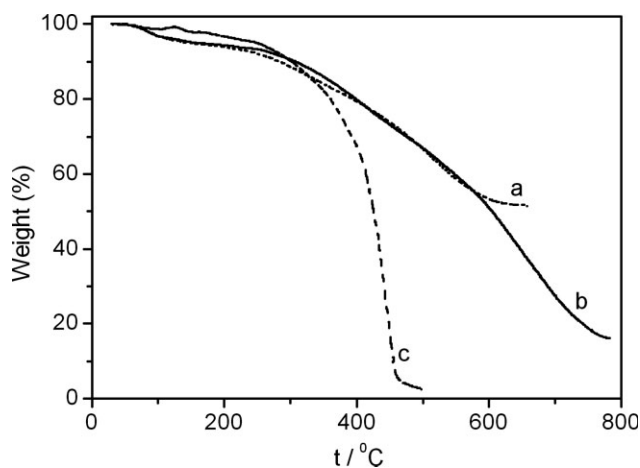
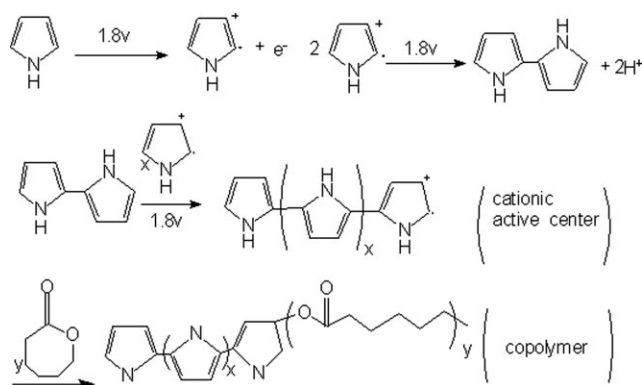


Figure 7 TGA curves obtained at $10^\circ\text{C}/\text{min}$ under nitrogen for (a) PPy, (b) Py-CL copolymer prepared potentiostatically at 1.8 V in CH_3NO_2 containing 0.1M Py, 1.5M CL, and 0.05M Bu_4NBF_4 , and (c) PCL.



Scheme 1 Possible mechanism of the electrochemical copolymerization of Py and CL in nitromethane solution.

Figure 7 shows a comparison on the TGA of PPy, PCL Py-CL, and copolymer. While PPy showed a residue of 70% weight retention at 500°C [Fig. 7(a)], PCL was completely degraded at that temperature [Fig. 7(c)]. The copolymer was resistant to heating up to 300°C , after which they lost weight rapidly [Fig. 7(b)]. The Py-CL copolymer showed an intermediate behavior between that of pure PPy and PCL.

Mechanism of electrochemical copolymerization of Py and CL

A possible mechanism for the copolymerization of Py and CL is proposed as shown in Scheme 1. It is well known that Py can be electrochemically oxidized to cation radicals or anion-combined cation radicals,³⁷ which then homopolymerizes and forms a polymer on the surface of electrode. CL cannot be electrochemically polymerized under the given experimental condition, but it can be attacked by reactive species and ring-opening polymerization takes place.³⁸ Cationic species produced by the oxidation of Py in solution probably initiates the polymerization of CL, resulting in the formation of Py-CL block copolymer.

CONCLUSIONS

The copolymerization of Py and ϵ -caprolactone was successfully carried out by a convenient one-step electrochemical method. The product was proved to be a copolymer of Py and ϵ -caprolactone, but not a composite or a blend of PPy and PCL. The Py-CL copolymer exhibited better mechanical properties than PPy. The existence of PCL matrix in copolymer was desired to improve the biocompatibility of polymer film. Thus, the copolymer film can be used for a good immobilization material of enzymes and the

construction of electrochemical biosensors. Further work is in progress.

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